

EXAFS and XANES of plutonium and uranium edges from titanate ceramics for fissile materials disposition

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Introduction

We report x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectra from the plutonium LIII and uranium LIII edges in prototype titanate ceramic hosts for disposal of surplus fissile materials. The titanate ceramics studied are based upon the pyrochlore and zirconolite mineral structures. Production materials are expected to contain as much as 10.5 weight % plutonium (and other fissile actinides) and 20.9 weight % (natural or depleted) uranium. XANES analysis shows that the plutonium is present almost entirely as Pu (IV). The EXAFS real-space structure of plutonium shows a strong second-shell peak clearly distinct from that of PuO₂ due to coordination by titanium. The plutonium signature is consistent with substitution into the calcium site within the zirconolite and pyrochlore phases. In contrast, the uranium XANES shows characteristics of U(V), with the EXAFS signal showing a distinct oxygen coordination shell at 2.07 Å. The combined EXAFS and XANES are characteristic of pentavalent uranium in an octahedral site. Thus, the uranium appears to occupy the titanium sites in pyrochlore, which may explain the high total actinide loading possible in these materials.

Methods and Materials

Two versions of the ceramic were examined, representing pure and impure feedstocks of the fissile material. The chemical formulations of the baseline (A0) and high-impurity (A9) titanate ceramics studied are provided in Table 1. The starting materials for the samples were calcined in static air at 750 °C. The resulting powders were then cold pressed and sintered in flowing argon at 1350 °C for approximately four hours. The major phases in these ceramics are pyrochlore [A₂Ti₂O₇], zirconolite [ABTi₂O₇], Hf-bearing rutile (TiO₂), and brannerite [BTi₂O₆]. Here A = Ca, actinides (ACT), and rare earth elements (REE); and B = ACT, REE, Zr, and Hf. Additional minor phases may occur depending on waste loading, including uranium oxides and glassy phases. The glassy phases (and rutile) fill interstices between the major phases [1]. Both Hf and Gd are added to the ceramic formulation as neutron absorbers in order to satisfy a defense-in-depth concept for the waste form.

The EXAFS measurements were made at the Materials Research Collaborative Access Team (MR-CAT) undulator beamline at Argonne National Laboratory. Measurements were made in fluorescence mode with the incident intensity ionization chamber optimized for maximum current with linear response (~10¹⁰ photons detected /sec). The fluorescence ionization chamber was filled with xenon gas and produced a signal of ~10⁸ photons/sec above the absorption edge. A double-crystal Si(111) monochromator with resolution of better than 4 eV at 20 keV was used in conjunction with a Pt-coated mirror to minimize the presence of harmonics. The counting time at each measured wavelength ranged from 2-8 seconds/point in the EXAFS region. We used the program *feffit* from the University of Washington package to fit the spectra and *feff* (version 8.00) to generate the x-ray scattering paths [2].

Table 1: Ceramic compositions in weight percent.

Compound	Specimen Type	
	A0	A9
CaO	9.95	9.44
TiO ₂	35.87	34.04
HfO ₂	10.65	10.11
Gd ₂ O ₃	7.95	7.54
UO ₂	23.69	22.48
PuO ₂	11.89	11.28
Al ₂ O ₃	-	0.50
MgO	-	0.44
CaCl ₂	-	0.66
Ga ₂ O ₂	-	0.57
Fe ₂ O ₃	-	0.15
Cr ₂ O ₃	-	0.08
NiO	-	0.13
CaF ₂	-	0.44
K ₂ O	-	0.32
Na ₂ O	-	0.14
MoO ₂	-	0.28
SiO ₂	-	0.46
Ta ₂ O ₅	-	0.19
B ₂ O ₃	-	0.17
WO ₂	-	0.49
ZnO	-	0.07

Results

The XANES analysis of plutonium LIII edge in the prototype ceramic demonstrates that it is almost entirely in the Pu(IV) oxidation state [3, 4]. The EXAFS analysis (Figure 1) demonstrates a coordination environment for plutonium in the ceramic that is different from PuO₂ [4]. The second shell coordination ($r = 3.59$ Å) environment from the EXAFS in the figure is due to titanium. The structure is consistent with Pu existing in the Ca site in the zirconolite or pyrochlore structure.

Examination of the XANES and EXAFS from the uranium LIII reveals substantially different behavior. The XANES signal (not shown) bears the signature of the relatively uncommon oxidation state U(V). The XANES of pentavalent uranium has been described by Farges [5] in a study of silicate glasses characterized by ultraviolet-visible spectroscopy and EXAFS/XANES. The EXAFS analysis (Figure 2) yields a first coordination shell at about 2.05–2.07 Å for both samples, further substantiating pentavalent uranium, as this is a characteristic length of a U(V)—O bond [6]. This surprising result may have implications for assumptions commonly made regarding valence in uranium-bearing titanate and niobate minerals.

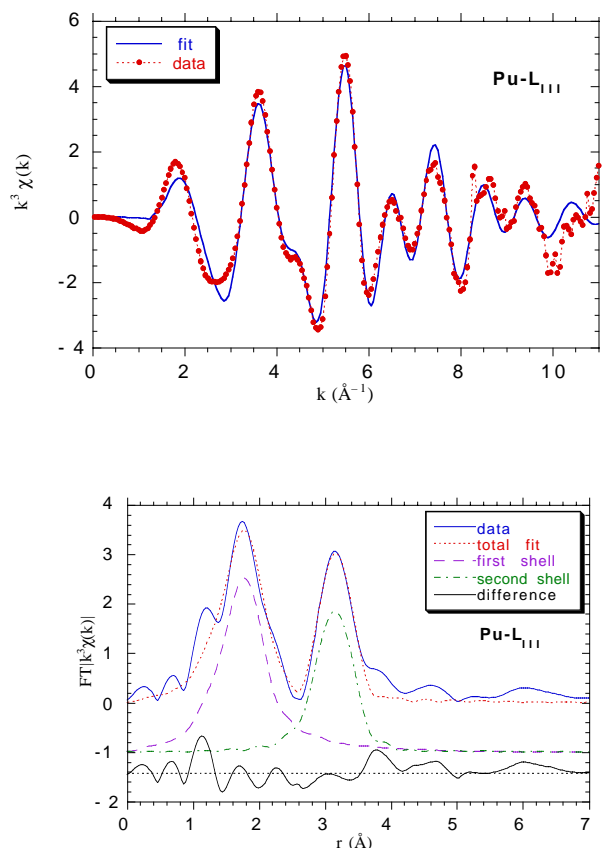


Figure 1: The plutonium LIII EXAFS data with fit (above) and real-space analysis of the coordination shells (below) from the A0 FMD ceramic.

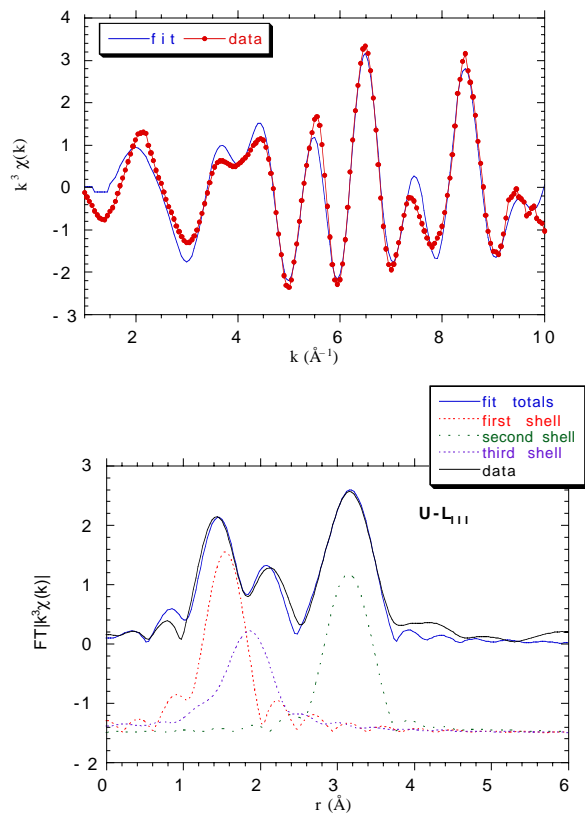


Figure 2: The uranium LIII EXAFS data with fit (above) and real-space analysis of the coordination shells (below) from the A9 FMD ceramic.

Discussion

Two formulations (A0 and A9) of the fissile materials disposition (FMD) ceramic were examined, and no significant difference appeared in the measured XANES and EXAFS of either uranium or plutonium. This indicates that the ceramic is robust as a waste form inasmuch as the crystal chemistry of the entrained actinides is insensitive to the presence of impurities in the feedstock (Table 1).

Pentavalent ions in titanium sites of pyrochlores and zirconolite are not uncommon. Indeed, certain end members of Nb(V) have been found in nature and synthesized in the laboratory. An analysis of the coupled substitutions required to introduce Me^{5+} ions to a titanium site is given by Gieré [7]. However, previous analyses (including that of Gieré [7]) have explicitly assumed that uranium would be quadravalent, residing in the calcium site. Our observations indicate that previous assumptions regarding uranium valence and site may be invalid. To date, only one natural mineral (wyartite) is reported to contain U(V) as an essential constituent [6]. Uranium-containing pyrochlores formed in an oxidizing environment appear to be likely candidates for pentavalent uranium.

Acknowledgments

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